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An NMR relaxivity and ESR study of the interaction of the paramagnetic manganese(II) and gadolinium(III) ions with anionic, cationic and neutral water-soluble polymers and their mixtures

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ABSTRACT

Solutions of the series of polymers (sodium polystyrene sulfonate, polyethyleneimine, and poly-N-vinylpyrrolidone) and certain mixtures thereof were studied by NMR relaxation and ESR spectroscopy using manganese(II) and gadolinium(III) ions as paramagnetic probes. The growth of the NMR-relaxation efficiency (relaxivity, $R_{1,2}$) is observed in solutions of the anionic polymer, as well as the decrease of $R_{1,2}$ - in the case of the cationic polymer. For mixtures of polymers, the dependent on the solution composition non-monotonic changes of $R_{1,2}$ are caused either by a formation of metal-interpolymer complexes or by a competitive cation/polymer substitution. For both ions, the changes in the ESR spectra of their polyelectrolyte solutions were analyzed. In case of sodium polystyrene sulfonate and blends thereof, the ESR spectra parameters are only slightly broadened compared to the pure metal aqua ion's, whereas for the polyethyleneimine solution the ESR spectra lines broaden greatly at pH > 7 up to their disappearance. All these effects were explained by the distinction of ion probes' binding mode to polyelectrolytes of different nature. Addition of NaCl to manganese(II) solutions containing polystyrene sulfonate, or mixtures thereof with PVP or PEI, lead to recovery of $R_{1,2}$ values, close to the probes' aqua ions relaxivities due to the release of the latter from the polymer/medium interface into the bulk water, while no changes were detected for PEI solutions.

1. Introduction

Aqueous solutions of polymers are the example of ultra microheterogenous media, which are characterized by the presence of the regions of different polarity on both parts of the polymer/bulk solution interface [1]. Meanwhile, other components of these solutions (ions and molecules) can be redistributed between these areas as they are affected by additional electrostatic or specific interaction with the fragments of macromolecules [2]. This should have a significant impact on the state of ions and molecules existing in such a solution, as well as on the reactions between the solution components. In particular, there may be a significant change in composition, structure and properties of the resulting compounds such as their optical, magnetic and other physical characteristics. Identification of the factors affecting interactions between metal ions or metal complexes and polymers (especially polyelectrolytes) can be used to solve a number of environmental and technological issues, for example, such as the development of functional polymer coatings [3,4], or in case of the polymer-enhanced ultrafiltration [5] - a prospect instrument for water purification from a low content of toxic metal ions, or vice versa, in order to reduce losses of valuable metals. Also, polyelectrolyte systems containing metal ions possess either catalytic activity in a number of reactions [6–8] or unique antibacterial properties [9]. One of the rapidly rising directions is the use of polymeric multilayer capsules as nanoreactors for synthesis of metal nanoparticles [8,10–11].

The state of ultra microheterogenous media may be successfully examined using the NMR relaxation method with paramagnetic probes (Gd(III), Mn(II) ions and their complexes) [12–15]. The choice of Gd^{3+} and Mn^{2+} cations as paramagnetic probes is caused by the fact that during their interaction with the larger particles (e.g. aggregate type surfactant micelles, vesicles, liposomes, and amphiphilic molecular receptors) the growth of relaxation efficiency $R_{1,2}$ is observed [16,17]. The latter is caused by retardation of the rotation of the probes upon their binding to mentioned aggregates. The $R_{1,2}$ increase occurs in the solutions of the paramagnetic cations, for which the relaxation time is controlled by the rotational correlation time, τ_r [12]. Previously Gd^{3+} and Mn^{2+} ions have been shown to be applicable as NMR probes to

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